PITT | SWANSON ENGINEERING

Center for ENERGY

A University Center within the Swanson School of Engineering

New Lamination and Doping Concepts for Enhanced Lithium – Sulfur Battery Performance

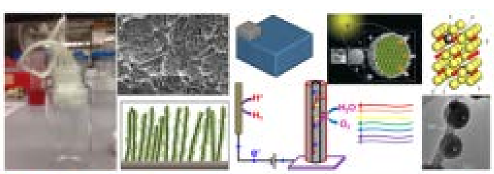
Prashant N. Kumta

Swanson School of Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania

Project ID #ES279

2017 DOE Vehicle Technologies Program Review

June 5-9, 2017



NECST lab Driving innovation in battery and fuel cell materials

Nanomaterials for Energy Conversion & Storage Technology

Overview

Timeline

Start date: October 1, 2014

End date: September 30, 2017

Percent complete: 85%

Budget

- Total project funding: $1,250,061
  - DOE share: $1,250,061
  - Contractor share: $ 0
- Funding received in FY 2016: $416,687
- Funding for FY 2017: $416,687

Barriers addressed

- Low achievable energy density
- Polysulfide dissolution
- Cycling Stability
- Electronic conductivity
- Poor rate capability
- Surface passivation of both anodes and cathodes

Partners

- UPitt (D. K. Achary)
- A. Manivannan (Global Pragmatic Materials)
- Kurt J. Lesker Co. (KJL)
- Complete Solutions (Technology Translation)

Project Objectives: Overall

Energy Storage Performance Requirements		Electric Vehicle
Characteristics	Unit	
Specific Discharge Pulse Power	W/kg	700
Discharge Pulse Power Density	W/l	1,500
Specific Regen Pulse Power	W/kg	300
Recharge Rate	kW	1.4
Specific Energy	Wh/kg	350
Energy Density	Wh/l	750
Calendar Life	Year	15
Cycle Life	Cycles	1,000
Operating Temperature Range	°C	-30 to +52

- Synthesis and characterization of suitable LIC matrix materials and multilayer composite sulfur cathodes
- Development of LIC coated sulfur nanoparticles
  - Scale up of high capacity engineered LIC coated multilayer composite electrodes
- Modification strategies for improving electronic conductivity of sulfur
- Advanced high energy density, high rate, extremely cyclable cell development
- First principles calculations for LIC and dopant materials identification

Project Objectives: 2016-17

Development of LIC coated sulfur nanoparticles, scale up of high capacity engineered LIC coated multilayer composite electrodes and doping strategies for improving electronic conductivity of sulfur

- Develop interface engineering concepts and coating strategies of Phase-1 materials to generate conductive carbon based multilayer composite electrodes of sulfur cathode
- Design and engineering of high capacity LIC coated sulfur nanoparticles for generation of high capacity materials for targeted energy density and 4 mAh cell
- Synthesis of doped sulfur nanoparticles with high electronic conductivity to reduce additive weight and increase energy density

Milestones-FY 2016/17

Date	Type	Description	Status
January 2016	Milestone	Fundamental electrochemical study to understand the interface electrochemical properties such as change of charge transfer resistance, Li^+ diffusivity and electronic conductivity	Completed
July 2016	Milestone	Develop interface engineering concepts and coating strategies of Phase-1 materials to generate carbon based multilayer composite electrodes of sulfur cathode	Completed
October 2016	Milestone	Synthesis of doped sulfur nanoparticles with high electronic conductivity to reduce additive weight and increase energy density.	Completed
October 2016	Go/No-Go	Design and engineering of high capacity LIC coated sulfur nanoparticles for generation of high capacity materials for targeted energy density and 4 mAh cell	Completed
April 2017	Milestone	Generation of integrated doped nanoparticulate sulfur-carbon-LIC composite electrode	Completed
October 2017	Milestone	Cost analysis of the integrated electrode (I.E.) electrodes, electrolytes, separators, binders, and related processes	On-going
October 2017	Milestone	Prismatic/pouch-type full cell assembly of I.E. with optimum thickness	On-going
October 2017	Milestone	Cell testing	On-going

Approaches/Strategies

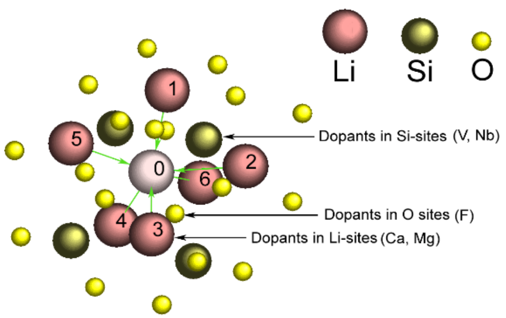
2016 April	May	June	July	Aug	Sep	Oct	Nov	Dec	2017 Jan	Feb	Apr
Develop interface engineering concepts and coating strategies of Phase-1 materials to generate carbon based multilayer composite electrodes of sulfur cathode				**Test results**							
		Synthesis of doped sulfur nanoparticles with high electronic conductivity to reduce additive weight and increase energy density.		Composite polymer electrolyte coatings		Directly doped sulfur assembly development				Generation of integrated doped nanoparticulate sulfur-carbon-LIC composite electrode	
Composite and framework approach						**Testing progress**				**Establishing and optimizing techniques**	

Go/ No – Go decision point: The Go/ No – Go point was demonstrated by generation of LIC coated sulfur nanoparticles with targeted energy density and 4 mAh cell

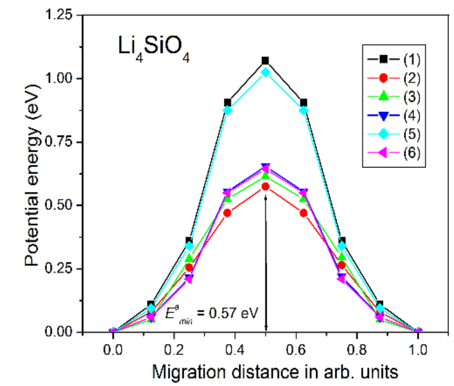
Challenges and barriers: Techniques for effective LIC lamination of thick electrodes (> 10 mg/cm^2) and of sulfur nanoparticles is currently ongoing

Technical Accomplishments: Theoretical Study – Improving Ionic Conductivity

- **Introduction of dopants inducing formation of Li^+-vacancies could improve the ionic conductivity**
- **One Li^+-vacancy can be created by :**
- **substitution of aliovalent cation on Li-site/Si-site/O-site with formula $[Li_{4-2x}[D]_x] SiO_4$; $[Li_{4-x} [D]_x Si_{1-x}] O_4$; $Li_{4-x}Si [O_{4-x}[D]_x]$**
- **Effect of doping on the activation barriers have been studied**
- Using the nudged elastic band method implemented in VASP (Vienna ab-initio simulation package), various Li-ion migration pathways have been considered and corresponding activation barriers E_a have been calculated

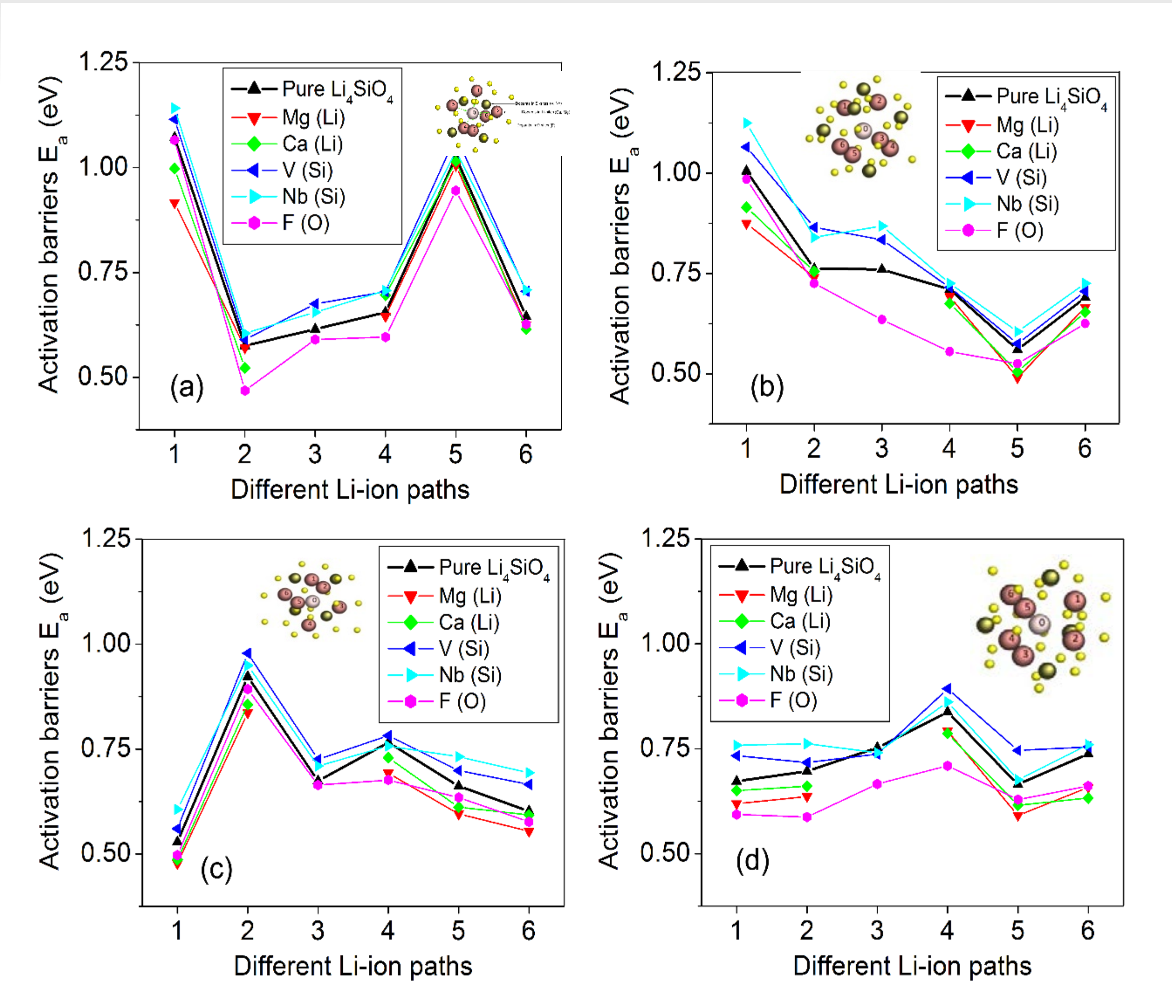


Activation barriers E_a (in eV) for different migration paths of Li-ions in pure and doped Li_4SiO_4 with various atomic configurations of dopants



Potential energy for different migration paths of Li-ions in pure Li_4SiO_4

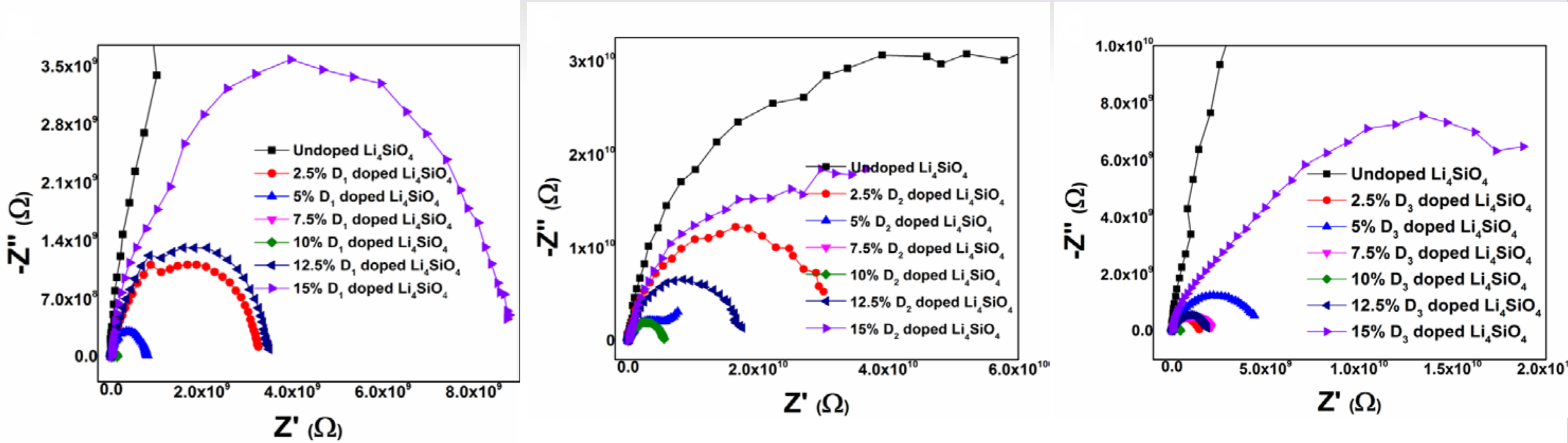
Technical Accomplishments: Doped Li_4SiO_4- diffusion pathways



- E_a decreases for Mg, Ca, and F but increases for V and Nb

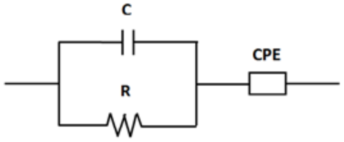
- All dopants create Li-vacancies which should improve an overall ionic conductivity

Technical Accomplishments: Effect of dopants on conductivity

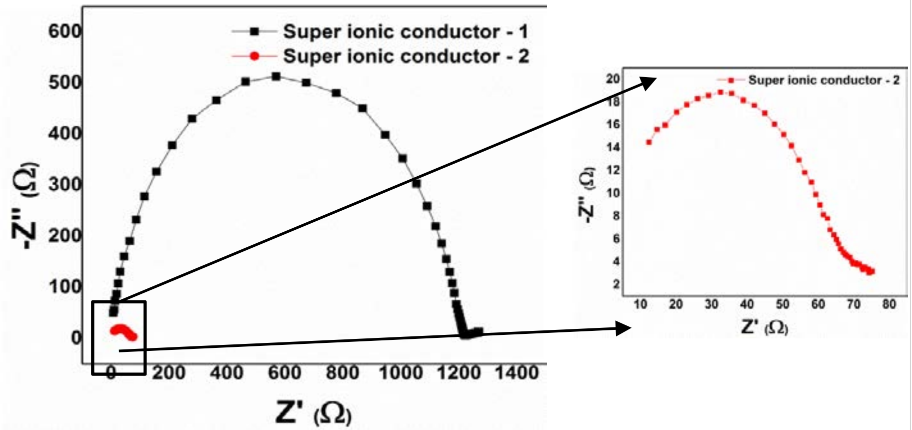


Impedance plots of various doped Lithium Orthosilicate

- **Dopants help reduce impedance by several orders**

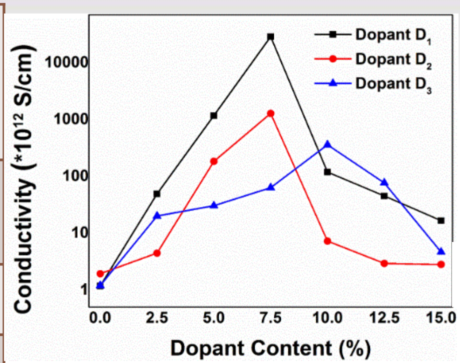


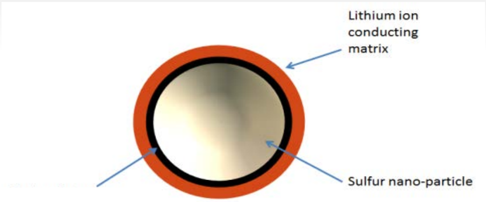
Equivalent circuit used to fit the impedance data



Technical Accomplishments: Effect of doping on conductivity

	D_1 doped ($\times10^{12}$ S/cm)	D_2 doped ($\times10^{12}$ S/cm)	D_3 doped ($\times10^{12}$ S/cm)
Li_4SiO_4 - undoped	1.16	1.29	1.19
2.5% doped	49.13	4.44	20.04
5% doped	1169.55	183.51	30.41
7.5% doped	28706.06	1277.59	63.13
10% doped	119.26	7.22	359.62
12.5% doped	45.08	2.93	76.95
15% doped	16.53	2.80	4.66

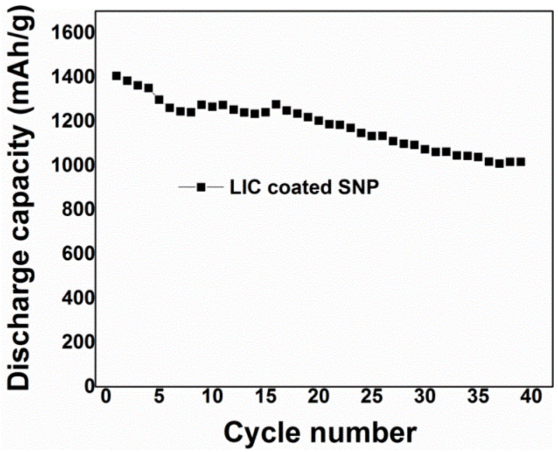




Interlayer

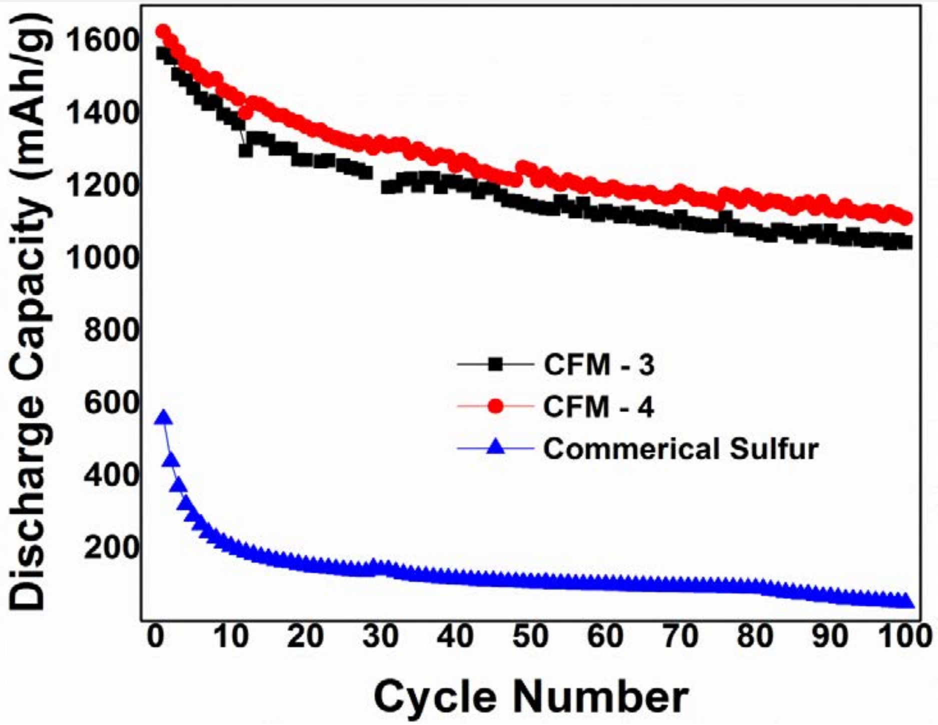
Li Ionic Conductivity as a function of Li Vacancy

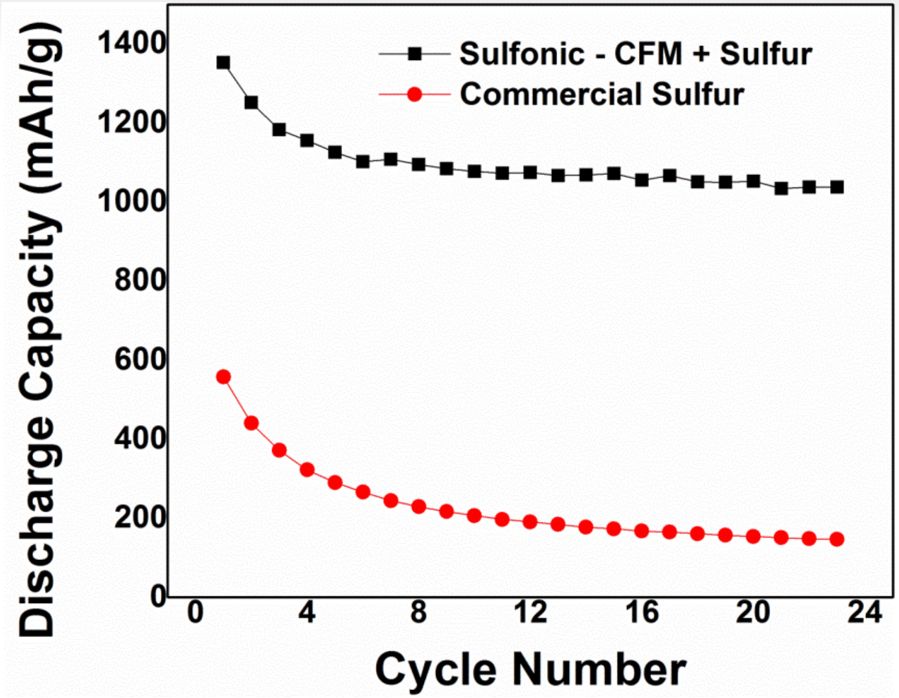
Conductive coatings on sulfur nanoparticles prevent polysulfide dissolution on a particle level



- **D_1, D_2 and D_3 doping increases the ionic conductivity of Li_4SiO_4**
- **7.5% D_1 doping gives four order increase in conductivity**
- **7.5% D_2 doping gives three order increase in conductivity**
- **New superionic conductors developed having conductivities of 0.153 mS/cm and 2.53 mS/cm matching liquids**

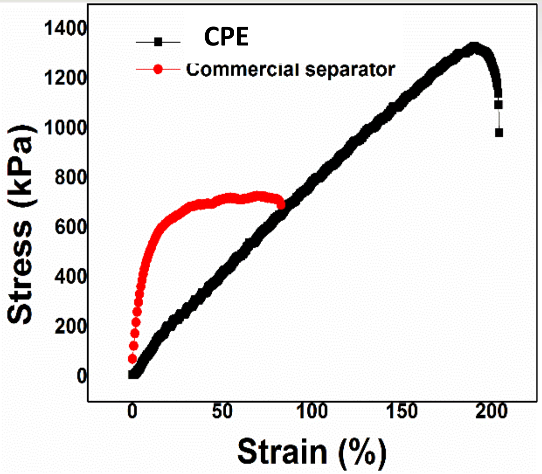
Technical Accomplishments: Gen-2 framework materials with no initial capacity loss

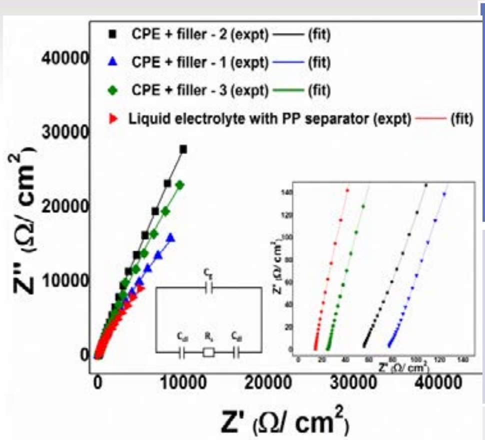




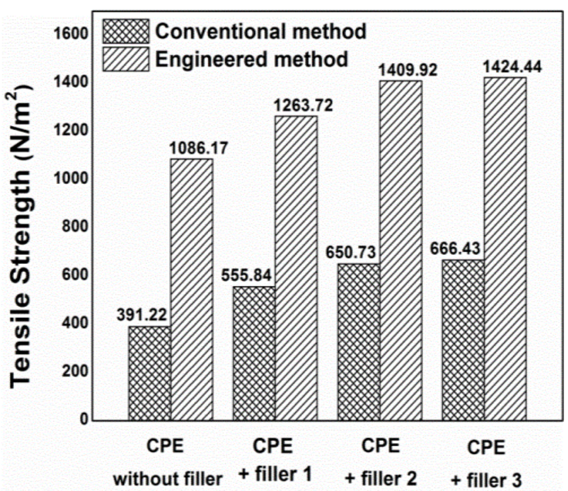
- Improvement in cycling stability of sulfur cathodes by use of Gen-1 CFM materials
  - Initial capacity loss due to framework interaction with sulfur
- Initial capacity loss is prevented and cycling stability is improved by use of Gen-2 CFM materials

Technical accomplishments: Composite Polymeric Electrolyte (CPE) membranes as LICs





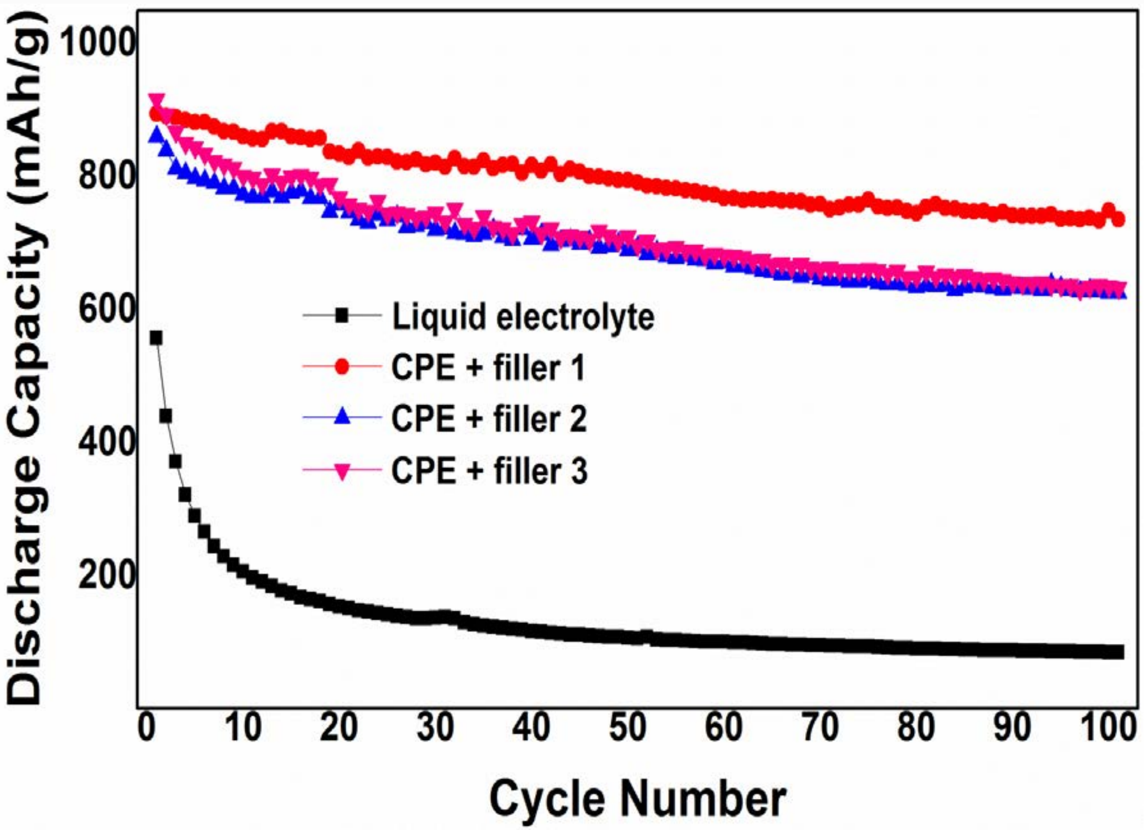
Sample Composition	Conductivity (S/cm)	Electrolyte uptake after 10 min (%)	Electrolyte uptake after 30 min (%)	Electrolyte uptake After 60 min (%)
Commercial separator with liquid electrolyte	$1.283 \cdot 10^{-3}$	436.67	550	551.5
CPE with filler 1	$1.881 \cdot 10^{-3}$	182.5	190.5	190.5
CPE with filler 2	$3.009 \cdot 10^{-3}$	207.5	219	220
CPE with filler 3	$9.4749 \cdot 10^{-3}$	253.5	266.5	270
Commercial PP separator		59.5	63	63



CPEs show superior mechanical stability and tensile strength as compared to commercial separators

- Liquid electrolyte separators degrade due to swelling upon excess uptake
- CPE separators demonstrate higher ionic conductivity due to superior uptake and mechanical stability in addition to conductive channels created by fillers

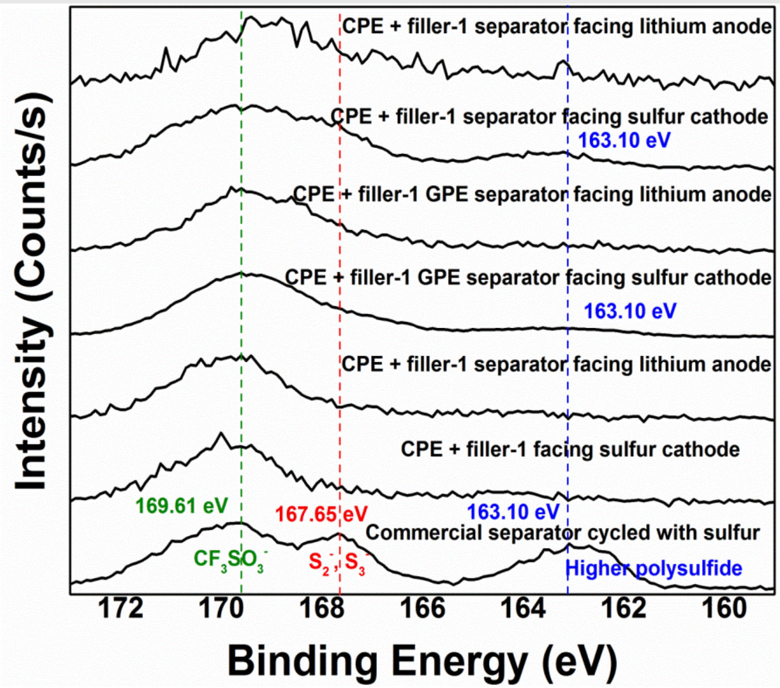
Technical Accomplishments: Gel-polymer electrolytes

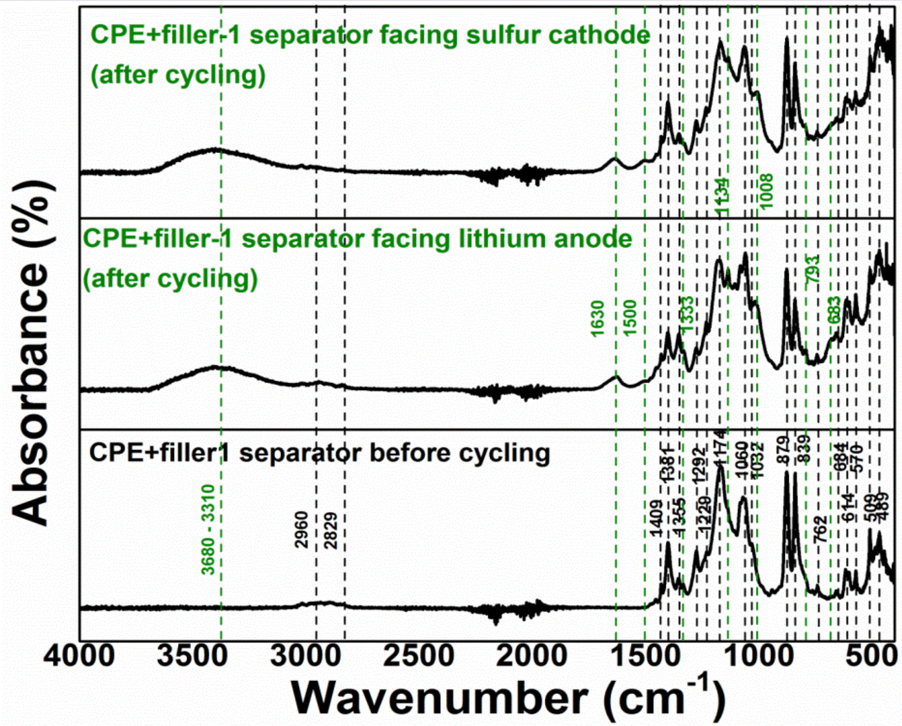


High stability with commercial sulfur which cycles very poorly in liquid electrolytes

High capacity sulfur materials are being tested to show stability at much higher capacities

Technical Accomplishments: Gel-polymer electrolytes

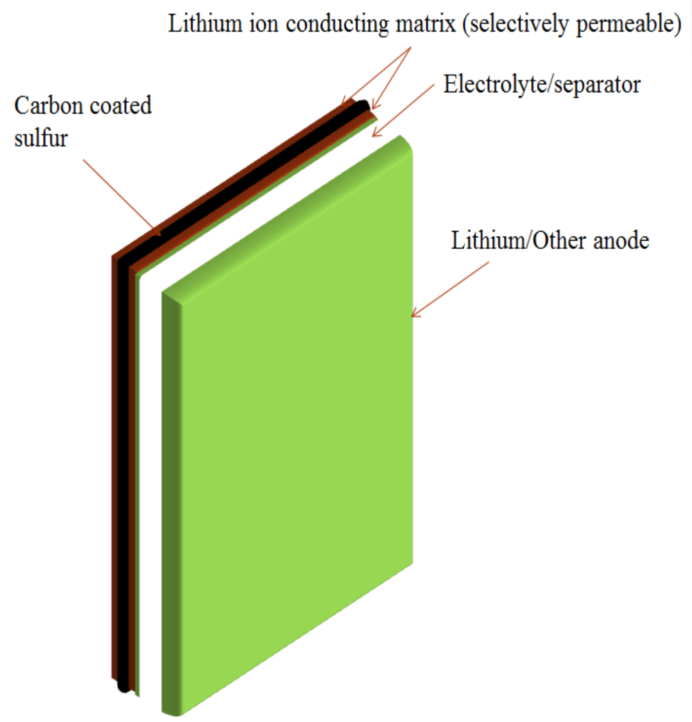


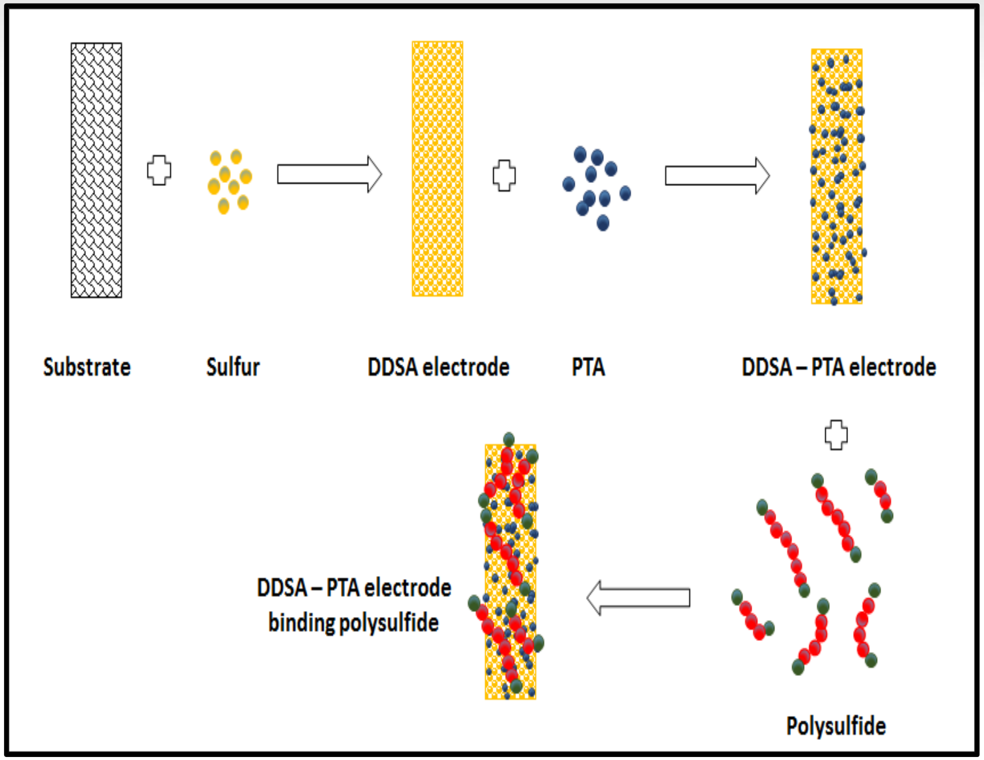


- CPE separators show absolutely no higher order polysulfides trapped therein unlike commercial liquid electrolyte separators after 100 cycles

- The FT-IR spectra of CPE before and after electrochemical cycling (100 cycles) is shown in the figure
- The FT-IR analysis shows that the chemical nature of the CPE is not destroyed upon cycling
- The CPEs are stable under electrochemical cycling

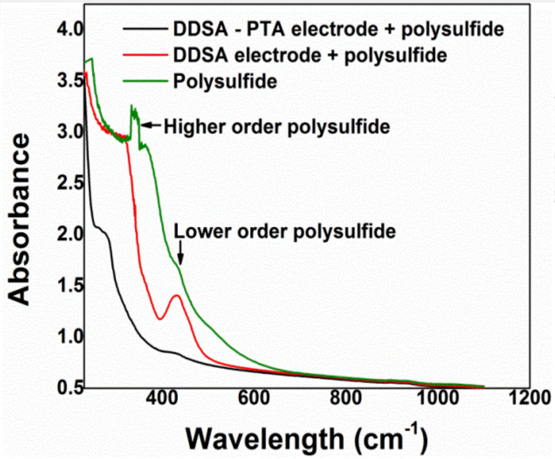
Technical Accomplishments: Directly doped sulfur architectures (DDSA) electrode with polysulfide trapping agent (PTA)

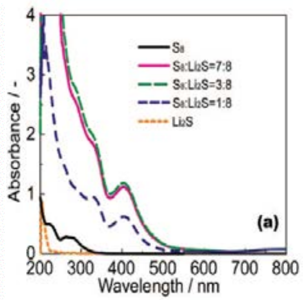


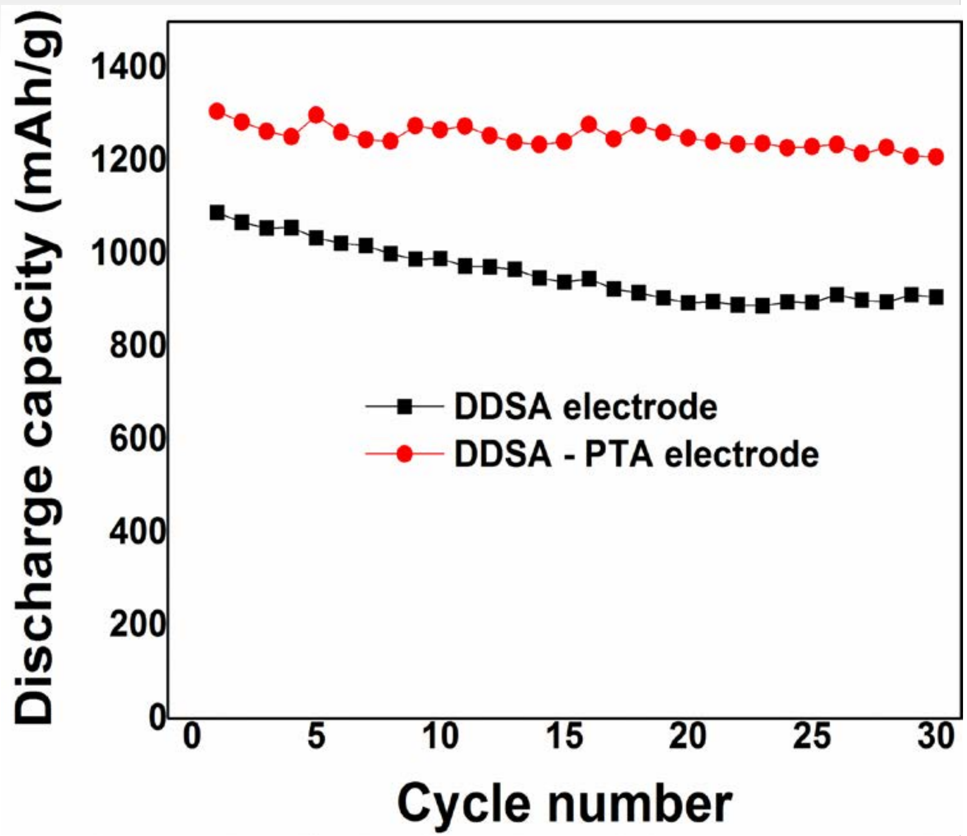


- High loading>15 mg/cm^2 3-D sulfur cathodes
- Conductive nanodots add to capacity significantly and act as PTAs

Technical Accomplishments: Thick 3-D sulfur DDSA electrodes



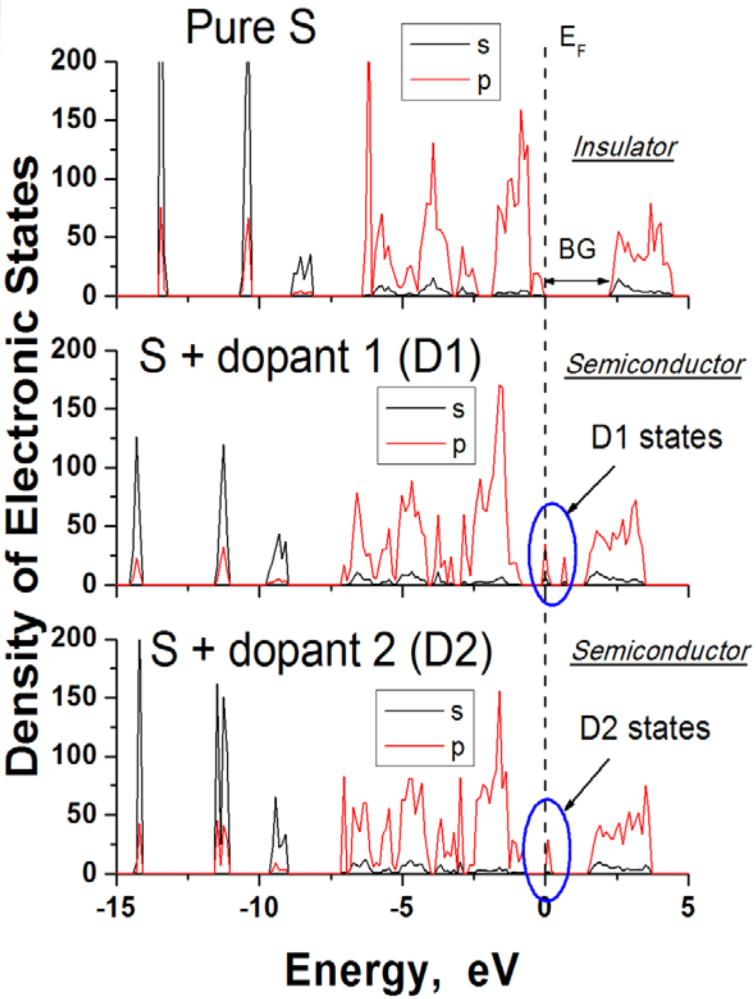




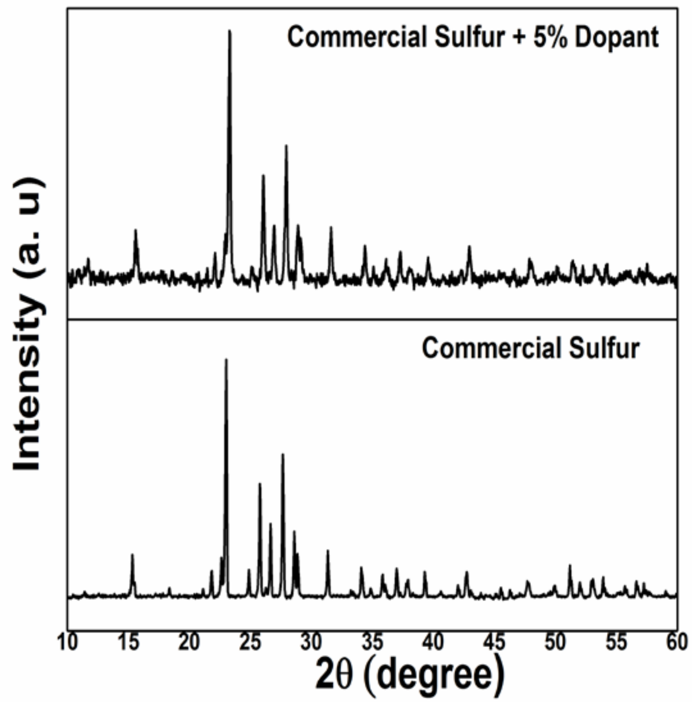
- The UV-visible spectrum peaks corresponding to the higher order polysulfide decreases in DDSA electrode due to binding of polysulfide
- The DDSA – PTA electrode shows strong binding of polysulfide and hence disappearance of polysulfide peaks

*Journal of The Electrochemical Society, 160 (8) A1304-A1310 (2013) 0013-4651/2013/160(8)/A1304/7

Technical Accomplishments: Electronic modification of Sulfur



First principles driven alteration of electronic states of sulfur to improve electronic conductivity



Responses to Previous Year Reviewers' Comments

There were no previous reviewer comments in 2016.

Collaboration and Coordination with Other Institutions

Collaborators (outside the VT Program):

- Dr. D. Krishnan Achary (University of Pittsburgh): for solid-state nuclear magnetic resonance (MAS-NMR) characterization
- A. Manivannan (Global Pragmatic Materials): Materials characterization using XPS studies
- Kurt J. Lesker Co. (KJL): Thin film deposition and vacuum techniques
- Complete Solutions: Technology Translation

Remaining Challenges and Barriers

- **Challenges**
  - Demonstration of full-cell performance for 1000 cycles
  - Demonstration of electrode-level capacity and decrease in additive content
- **Barriers**
  - No significant barriers to proposed work have been encountered thus far
  - Possible barriers include accounting for scaling of performance and increasing sulfur weight percentage in electrodes
  - Lithium-metal anode based batteries fail to cycle over extended cycling due to dendrite structure formation and separator puncture in the case of commercial separators
- **Solutions**
  - Use of CPEs eliminates problem of separator puncture ensuring that long cycling will be demonstrated in full cells
  - Doping of sulfur in DDSA electrodes helps increase sulfur weight percentage to >80%
  - Lithium metal anode based full cells will cycle for 1000 cycles using novel anodes will be developed as part of DOE-EERE-OVT-ES-327

Proposed Future Work

Large electrode fabrication and testing

Final deliverable of >4 mAh cell

Upcoming key milestones

October 2017	**Prismatic/pouch-type full cell assembly of I.E. with optimum thickness**	**On-going**
October 2017	Cell testing complete and deliverable >4 mAh full cells	On-going

Any proposed future work is subject to change based on funding levels

Summary

Cycling characteristics of various sulfur battery systems synthesized and evaluated in this work.			
Materials	Initial discharge capacity (mAh/g-S)	Initial capacity fade¥ (% capacity)	Fade rate*(% capacity/cycle)
LIC coated SNPs	1384.7	14.30	0.0088
Sulfur CFM-2	1460.4	54.79	0.012
Sulfur CFM-3	1565.5	14.65	0.0033
Sulfur CFM-4	1625.3	13.15	0.0031
Sulfur IFM	1012.7	9.09	0.0017
CPE with filler-3	860.1	6.70	0.0027
DDSA electrode with PTA	1305	4.26	0.0014

¥Fade rate calculated on the basis of 1st cycle capacity and 5th cycle capacity.

- Demonstrated sulfur cathodes with very high capacities and exceptionally low fade rates of <0.01%/cycle
- Cycling behavior demonstrated for up to 300 cycles with further cycling tests ongoing

Any proposed future work is subject to change based on funding levels

Publications and Presentations

- Shanthi, P.M.; Jampani, P.H.; Gattu, B.; Sweeney, M.; Datta, M.K.; Kumta, P.N. **Understanding the Origin of Irreversible Capacity loss in Non-Carbonized Carbonate− based Metal Organic Framework (MOF) Sulfur hosts for Lithium− Sulfur battery**, *Electrochimica Acta* Vol. 229, pp. 208-218 (2017)
- Jampani, P.H.; Gattu, B.; Shanthi, P.M.; Damle, S.S.; Velikokhatnyi, O.I.; Datta, M.K.; Damle, S.S.; Basson, Z.; Bandi, R.; Datta, M.K.; Park, S. ; Kumta, P.N. **Flexible sulfur wires (Flex-SWs) – A new versatile platform for lithium-sulfur batteries**, *Electrochimica Acta*, Vol. 212, pp. 286-293 (2016)
- Jampani, P.H.; Gattu, B.; Velikokhatnyi, O.I.; Datta, M.K.; Damle, S.S.; Kumta, P.N. **Heterostructures for improved stability of Lithium sulfur batteries**, *Journal of the Electrochemical Society*, Vol. 161, pp. A1173-A1180 (2014)
- Shanthi, P.M.; Jampani, P.H.; Gattu, B.; Velikokhatnyi, O.I.; Kumta, P.N. **Doped Lithium Orthosilicates - Promising High Rate Lithium-Ion Conductors for Li-S Batteries**, *The Electrochemical Society* (Fall 2016), Honolulu, HI
- Gattu, B.; Shanthi, P.M.; Jampani, P.H.; Velikokhatnyi, O.I.; Kumta, P.N. **Highly Ordered Complex Framework Materials (CFMs) As Sulfur Hosts for Li-S Batteries**, *The Electrochemical Society* (Spring 2016), San Diego, CA
- Jampani, P.H.; Shanthi, P.M.; Gattu, B.; Kumta, P.N. **Novel Flexible Sulfur Wire Fabrics (FSF) for Lithium-Sulfur Batteries**, *The Electrochemical Society* (Spring 2015), Chicago, IL
- Shanthi, P.M.; Jampani, P.H.; Gattu, B.; Velikokhatnyi, O.I.; Kumta, P.N. **Effect of Coating and Particle Properties on the Cycling Stability of Li-Ion Conductor (LIC) Coated Sulfur Cathodes**, *The Electrochemical Society* (Spring 2015), Chicago, IL
- Gattu, B.; Jampani, P.H.; Datta, M.K.; Kumta, P.N. **Nanostructured Sulfur and Composites for Lithium-Sulfur Batteries**, *The Electrochemical Society* (Spring 2014), Orlando, FL
- Jampani, P.H.; Gattu,B.; Velikokhatnyi, O.I.; Kumta, P.N. **Novel Heterostructures for Lithium-Sulfur Batteries**, *The Electrochemical Society* (Spring 2014), Orlando, FL
- Jampani, P.H.; Gattu, B.; Shanthi, P.M.; Kumta, P.N. **Novel electro-spun sulfur wires for fabricating mattes of lithium-sulfur batteries, International Patent Number: WO 2016/145429 A1**, U.S. Provisional Patent, Application Number: PCT/US2016/022283 (Filing date: 03/14/2016)

Technical Back-Up Slides

Technical Accomplishments: Li-diffusivity in doped Li_4SiO_4

Temperature dependence of diffusion coefficient could be estimated from:

$$D(T) = a^2 v^* \exp \{ -E_a/k_b T \},$$

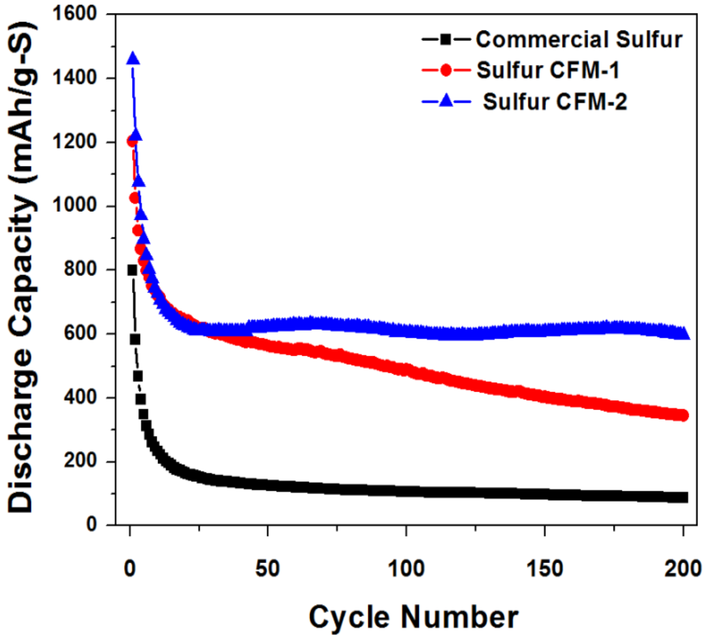
D – diffusion constant
a – the hopping distance (~ 3.0 Å in this case)
v^* – hopping frequency (~ 10^{13} s^{-1})

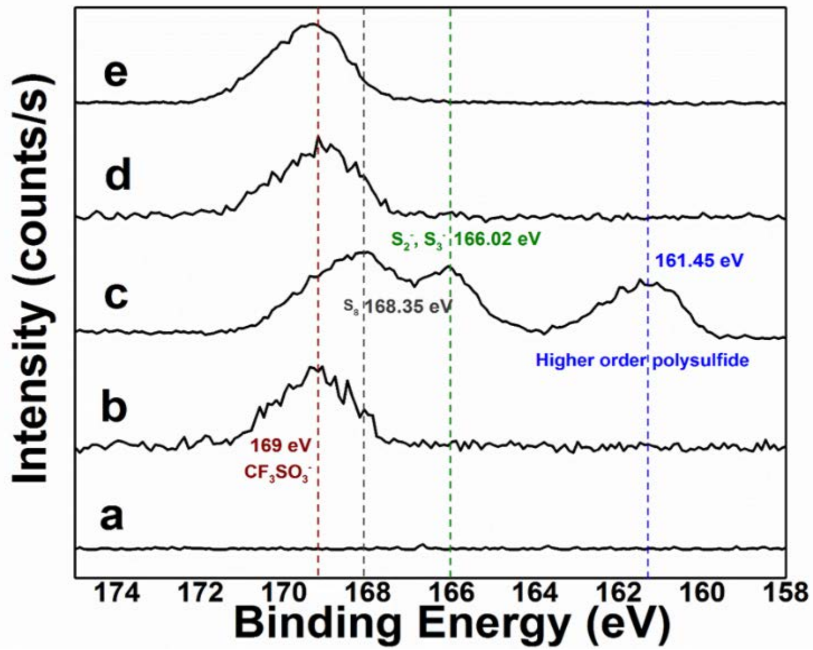
Assuming minimum E_a = ~ 0.6 eV from E_a calculations,

For T = 25 ^{0}C	D = ~10^{-12} cm^2/s
For T = 500 ^{0}C	D = ~10^{-6} cm^2/s
For T = 1000 ^{0}C	D = ~10^{-3} cm^2/s

Also, doping increases the Li-ionic conductivity on 2-3 orders in comparison to pure Li_4SiO_4 confirming experiments with theoretical calculations.

Technical Accomplishments: Gen-1 Framework materials

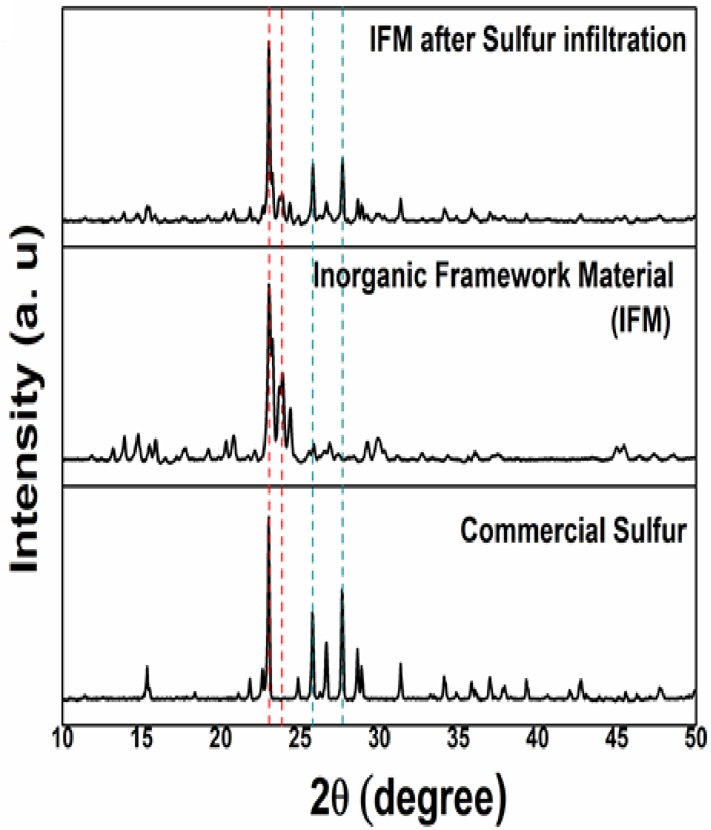


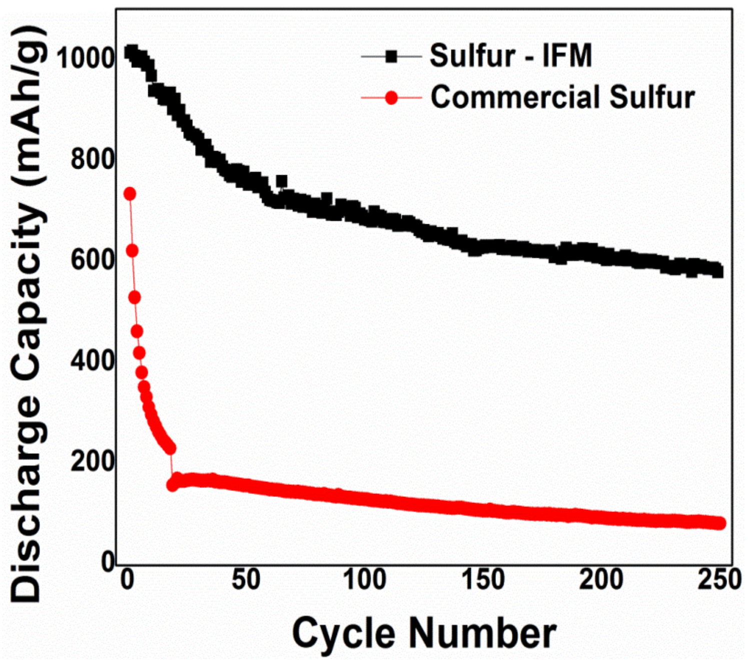


- ➢ Improvement in cycling stability of sulfur cathodes by use of Gen-1 CFM materials
- ➢ Initial capacity loss due to framework interaction with sulfur

XPS S2p Binding Energy profile of a) commercial separator b) commercial separator soaked in electrolyte; separators of c) commercial sulfur electrode d) Sulfur CFM-1 e) Sulfur CFM-2 electrodes; (after 200 cycles at 0.2 C rate)

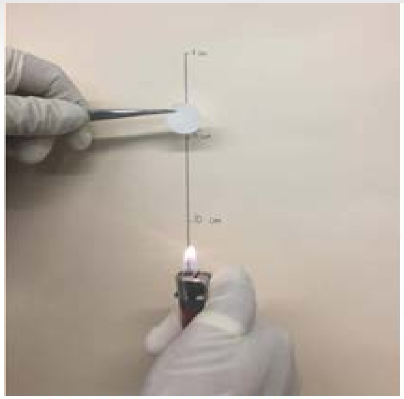
Technical Accomplishments: Inorganic Framework Materials (IFM)



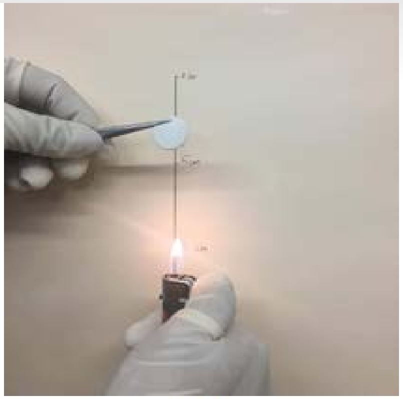


Porous framework materials demonstrate low fade rate (0.0017%/cycle)

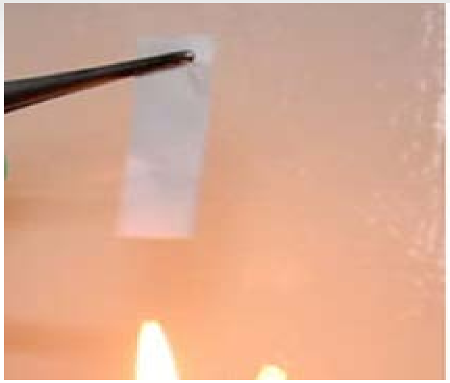
Technical accomplishments: New Flame resistant CPEs



Commercial separator
exposed to heat

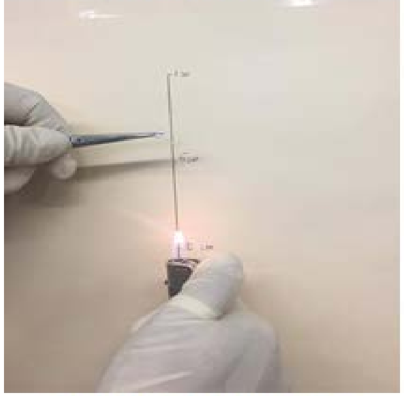


CPE
exposed to heat

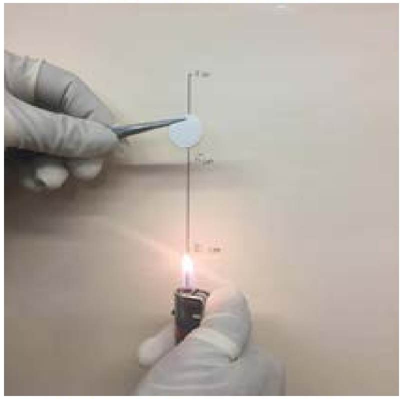


Commercial battery separator

CPE battery separator

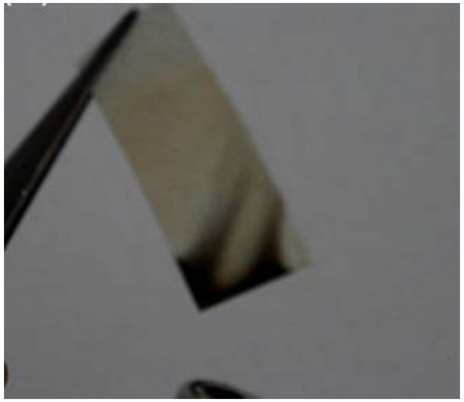


Commercial separator
shrinking within 5 secs



CPE unaffected by heat
for over 60 sec

Commercial battery separator
upon exposure to fire



CPE battery separator upon
exposure to fire